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Primary and Secondary Crystallization in the Blend of Poly(L-lactic acid) and Poly(D-lactic acid)

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1 Introduction

In recent years, poly(lactic acid) (PLA) gained a high popularity as a potential replacement for conventional plastics. Being biodegradable, non-toxic and made of renewable materials gives PLA many beneficial qualities; however, improving its mechanical and thermal properties remains a challenge. One way of improving these properties is by promoting stereocomplex crystallites (SC) formation in PLA. Pure PLA has two enantiomers, L-lactic acid (PLLA) and D-lactic acid (PDLA). These two enantiomers can form stereocomplex crystallites that have a melting temperature higher by almost 50°C as compared to their respective homo crystallites (HC). To better understand the mechanism of stereocomplex and homo crystallites formation, primary and secondary crystallization of PLA were examined in this study, by means of differential scanning calorimetry (DSC), polarized optical microscope (POM) observation, and wide-angle X-ray scattering (WAXS). The effects of isothermal crystallization experiments at different temperatures for different durations were investigated.

2 Experiment

The WAXS measurements at room temperature were carried out by using the synchrotron radiation as an X-ray source at the beamline BL-6A of Photon Factory at KEK (High-Energy Accelerator Research Organization) in Tsukuba, Japan. The wavelength of the incident X-ray beam was 0.150 nm. The specimens measured were in advance thermally annealed at 170 °C for 65 min., 3, and 5 hours. The scattering vector q was calibrated by using polyethylene for WAXS. Here, the magnitude of q is defined as, $|\boldsymbol{q}| = q = (4\pi/\lambda)\sin(\theta/2)$ with λ and θ being the wavelength of X-ray and the scattering angle, respectively. The background scattering was subtracted. The one-dimensional WAXS profiles was obtained by taking the sector average of the 2d-WAXS pattern.

3 Results and Discussion

The 1d-WAXS profile for the specimen thermally annealed at 170 °C for 5 hours showed crystalline peaks for both of SC and HC. This results suggest that the long annealing duration allows for secondary crystallization to take place for PLA, even at high temperatures, such as 170°C — a temperature previously thought to be too high for the formation of HC. In Figure 1, DSC results show three endothermic peaks upon heating to 250°C after the annealing duration, with the endothermic peak 1 at a temperature well above 185°C. This is a remarkably high temperature if ascribed to HC formation. However, for a short annealing duration, no endothermic peak at this temperature was observed. POM observation show that spherulites growth takes ~1h to fill the area of the specimen and DSC results confirmed that SC formation prevails at the initial phase of annealing. However, the continuation of isothermal crystallization would allow for further crystallites formation, albeit confined by the available limited space. The formed crystallites are assumed to be smaller in size, resulting in a lower melting temperature (peaks 1 and 2). Thus, it is presumed that given an appropriate isothermal crystallization temperature, SC (peaks 2 and 3) and HC (peak 1) can form as a result of primary and secondary crystallization in PLLA and PDLA blend, when annealed for long durations.

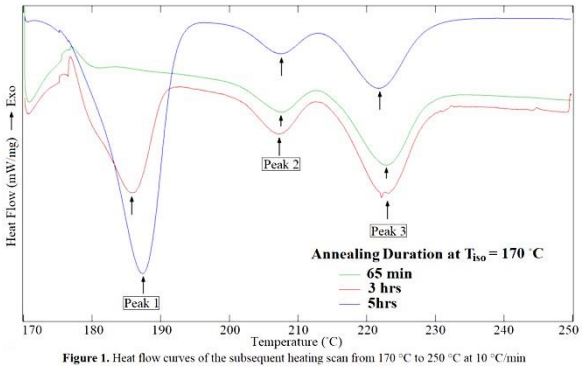

Figure 1. Heat flow curves of the subsequent heating scan from 170 °C to 250 °C at 10 °C/min

Fig. 1: DSC charts for the specimens isothermally at 170˚C for 65 min., 3, and 5 hours.

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